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THE DEPENDENCE OF MAGNETIC PROPERTIES ON STRUCTURE IN THE SYSTEMS--ETC(U)

AUG 82 M TELLESEN, R KERSHAW, K DWIGHT

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20. ABSTRACT (Continued)

When the nominal composition $\text{Fe}_2\text{Ge}_{0.3}\text{Si}_{0.7}\text{O}_4$ was pressed at 50 kb, the resulting product was predominantly a spinel phase. The magnetic properties for each composition crystallizing with the olivine structure were found to be consistent with the presence of strong anti-ferromagnetic $\sim 120^\circ$ B-O-B nearest-neighbor interactions. Both the spinel and the olivine structures have weaker $\sim 90^\circ$ B-O-B interactions.

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The Dependence of Magnetic Properties on
Structure in the System $\text{Fe}_2\text{Ge}_{1-x}\text{Si}_x\text{O}_4$

by

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INTRODUCTION

The orthosilicates of manganese, iron, cobalt, and nickel and manganese orthogermanates crystallize with the olivine structure, whereas the orthogermanates of iron, cobalt, and nickel crystallize with the normal spinel structure. In addition, the orthosilicates of iron, cobalt, and nickel have been reported to transform to the spinel structure at high pressure (1-3). The relationship between the olivine and spinel structure-types is of geological interest, and this has motivated several studies dealing with solid solutions between orthosilicate olivines and orthogermanate spinels (4-12). The solubility of the olivine Mg_2SiO_4 in the spinel Ni_2GeO_4 has been determined as a function of pressure (4,5). Extrapolation of the data from these studies gave the transformation pressure of pure Mg_2SiO_4 . At ambient pressure, Mg_2GeO_4 , which crystallizes with the olivine structure, can substitute to a large degree into the iron, cobalt, and nickel orthogermanate spinels (6-9). The compounds MnFeGeO_4 and MnCoGeO_4 have been reported to form olivines at ambient pressure and to undergo transformation to spinels at high pressure (10).

There have been several studies involving solid solution of orthosilicate olivines with the corresponding orthogermanate spinels of the same transition metal. Under ambient pressure, it has been reported that 20 mole percent of the olivine Ni_2SiO_4 can be substituted into the spinel Ni_2GeO_4 and 25 mole percent of the spinel will substitute into the olivine;

at 30 kb, complete solid solution in the spinel phase has been shown (11). Similarly, up to 50 mole percent of Fe_2SiO_4 has been reported to substitute into Fe_2GeO_4 at 40 kb (12).

Both the olivine Fe_2SiO_4 and the spinel Fe_2GeO_4 are reported to be antiferromagnetic, with low Néel temperatures (T_N) and negative Weiss constants (θ) (13-17). The reported values of θ for Fe_2SiO_4 (-150 and -125 K) were more negative than the values for Fe_2GeO_4 (-25 and -15 K). In this study, both the substitution of germanium for silicon in the olivine Fe_2SiO_4 and the substitution of silicon for germanium in the spinel Fe_2GeO_4 at high pressure were examined with respect to the effect upon the magnetic properties. For both the olivine and spinel compositions, it was anticipated that the physical properties may be related to the structure as well as to the extent of substitution.

EXPERIMENTAL

Sample Preparation. Polycrystalline samples of members of the system $\text{Fe}_2\text{Ge}_x\text{Si}_{1-x}\text{O}_4$ were prepared by the solid state reaction of stoichiometric mixtures of iron (Leico, 99.999%), Fe_2O_3 (Mapico Red, Columbian Carbon Co.), GeO_2 (Alfa Products, Ultrapure) and/or SiO_2 (General Electric Co., Type 214 Silica, 99.99%). Silicon dioxide powder was obtained from the pulverized silica tubing dried under vacuum at 800°C. Reaction mixtures were heated in evacuated silica tubes at 800°C for 48 hr, followed by two or more 48 hr intervals at 1000°C with intermittent grinding under N_2 atmosphere. Silica reaction tubes were presoftened before use to minimize attack.

High pressure synthesis was performed with the use of a belted anvil press described by Hall (18). Samples were ground thoroughly, moistened with water, and squeezed in Teflon holders with the application of full pressure before heating. At the end of a run, sample heating was stopped 15 min before the pressure was released. Pyrex holders were used when temperatures exceeded 500°C.

Sample Characterization. Powder diffraction patterns were obtained with the use of a Norelco diffractometer, employing monochromatic high-intensity $\text{CuK}\alpha_1$ radiation ($\lambda = 1.5405\text{\AA}$). Fast scans at $1^\circ (2\theta)/\text{min}$ were examined for the presence of impurity phases. Lattice parameters were determined by least-squares analysis of slow scans at $0.25^\circ (2\theta)/\text{min}$ in the range from 12 to $72^\circ (2\theta)$. Debye-Scherrer photographs were obtained for small samples, using $\text{FeK}\alpha$ radiation ($\lambda = 1.9360\text{\AA}$).

Magnetic susceptibility measurements were performed from 77 to 300 K using a Faraday balance described elsewhere (19). Magnetic field strengths between 6.22 and 10.40 kOe were employed, and the balance was calibrated with Pt wire ($\chi_g = 0.991 \times 10^{-6}$ emu/g at 275 K).

RESULTS AND DISCUSSION

The olivine Fe_2SiO_4 and the spinel Fe_2GeO_4 have the following equivalent site occupancies: silicon or germanium cations occupy tetrahedral A-sites and iron cations occupy octahedral B-sites. The structure-types can be described by the way AO_4 tetrahedra and BO_6 octahedra join together (20). The spinel structure consists of a three-dimensional network of straight

chains of edge-shared octahedra. Tetrahedra are isolated from each other, sharing only corners with octahedra. Figure 1 shows the arrangement of B-sites between and above two close-packed planes of O^{2-} anions in the spinel structure. Across shared edges, the B-O-B angle is nearly 90° , and the iron-iron distance in Fe_2GeO_4 is 2.97\AA .

In the olivine structure, edge-shared octahedra form serrated chains. Independent tetrahedra share edges and corners with octahedra and are aligned in rows which isolate the serrated octahedral chains within a given plane. Corner-shared octahedra link serrated chains in planes above and below. Figure 2 shows the arrangement of B-sites between and below two close-packed planes of O^{2-} anions in the olivine structure. The Fe-O-Fe angles across shared edges (within a chain) range from 92 to 98° in Fe_2SiO_4 , and the Fe-Fe distances across shared edges range from 3.05 to 3.31\AA . The Fe-O-Fe angles at shared corners (between chains) range from 114 to 128° (14).

For the antiferromagnetic compounds Fe_2SiO_4 and Fe_2GeO_4 , the Weiss constant (θ) may be considered a measure of the strength of the octahedral (B-site) interactions. The magnetic exchange contribution from a covalent B-O-A-O-B interaction involving diamagnetic A-site cations (16,21) is expected to be negligible. Likewise, the direct overlap of $Fe^{2+} t_{2g}$ orbitals across shared octahedral edges is expected to be small (22). For the $t_{2g}^4 e_g^2$ configuration of Fe^{2+} , both weak ferromagnetic and antiferromagnetic 90° B-O-B nearest-neighbor interactions are possible (23). For example, ferromagnetic coupling can occur via $t_{2g}-p\pi$ to $p\sigma-e_g$ bonds. In the olivine, $\sim 120^\circ$ B-O-B nearest-neighbor interactions are expected to be largely of $p\sigma-e_g$ character and, therefore, strongly antiferromagnetic.

The Compounds Fe_2SiO_4 and Fe_2GeO_4 . Fe_2SiO_4 and Fe_2GeO_4 were prepared under evacuated sealed tube conditions. Fe_2SiO_4 was a pale golden brown powder which crystallized with the olivine structure (space group Pbnm). The observed cell parameters listed in Table I compare well with the values in the literature (2,14). Fe_2GeO_4 was a dark brown powder which crystallized with the spinel structure (space group Fd3m). The observed cell constant is given in Table I and agrees with the values reported in the literature (9,17). The magnetic susceptibility data for both Fe_2SiO_4 and Fe_2GeO_4 (Figure 3) obey the Curie-Weiss law in the region of 90 to 300K. The Curie-Weiss parameters given in Table II were determined from least-squares fits. The μ_{eff} values of $5.22(2)\mu_B$ and $5.39(4)\mu_B$ for Fe_2SiO_4 and Fe_2GeO_4 , respectively, are slightly higher than the spin-only moment of $4.90\mu_B$, but lie well within the usual range of 5.2 - $5.5\mu_B$ for high-spin Fe^{2+} (24). The value of μ_{eff} for Fe_2GeO_4 agrees with those reported previously (15-17); the value for Fe_2SiO_4 differs from the $6.05\mu_B$ reported by Kondo et al. (13) and Santoro et al. (14) for their samples. The Weiss constant (θ) of $-87(1)\text{K}$ for Fe_2SiO_4 olivine is significantly more negative than the value of $-32(1)\text{K}$ for Fe_2GeO_4 spinel. This indicates that the antiferromagnetic interactions are stronger in Fe_2SiO_4 olivine than in Fe_2GeO_4 spinel.

The Solid Solution Series $\text{Fe}_2\text{Ge}_x\text{Si}_{1-x}\text{O}_4$. To determine the extent of solubility between Fe_2SiO_4 and Fe_2GeO_4 , mixed compositions were prepared under evacuated sealed tube conditions. The solubility of the olivine Fe_2SiO_4 in the spinel Fe_2GeO_4 was less than 10 mole percent. X-ray analysis indicated

that 20 mole percent of the spinel Fe_2GeO_4 could be substituted into the olivine Fe_2SiO_4 ; the 30 mole percent germanium composition resulted in a spinel-olivine mixture. Microscopic examination of all samples containing germanium revealed the presence of small dark brown particles, which are probably Fe_2GeO_4 spinel; the quantity present was too small to be detected by x-ray analysis. The orthorhombic cell parameters measured for the olivine solid solution series $\text{Fe}_2\text{Ge}_x\text{Si}_{1-x}\text{O}_4$ (where $0 \leq x \leq 0.2$) are listed in Table I. The cell volume (V) increases linearly with the germanium content, which indicates the existence of solid solutions.

The Curie-Weiss parameters for the $\text{Fe}_2\text{Ge}_x\text{Si}_{1-x}\text{O}_4$ system, listed in Table II, show a small increase in the magnitude of the Weiss constant upon substitution. The Curie-Weiss plot for the olivine $\text{Fe}_2\text{Ge}_{0.2}\text{Si}_{0.8}\text{O}_4$ is compared with those for the olivine Fe_2SiO_4 and the spinel Fe_2GeO_4 in Figure 4. Upon substitution of 20 mole percent germanium for silicon within the olivine structure, θ has a value of $-96(1)\text{K}$, remaining very close to $-87(1)\text{K}$ for pure Fe_2SiO_4 . This result agrees with the data reported in the literature for the olivines Mn_2SiO_4 and Mn_2GeO_4 . These compounds have identical Curie-Weiss parameters with $\mu_{\text{eff}} = 5.85\mu_B$ and $\theta = -163\text{K}$ (13,14,25). For the $t_{2g}^3 e_g^2$ configuration of Mn^{2+} , only antiferromagnetic nearest-neighbor interactions are expected. These antiferromagnetic interactions do not appear to be sensitive to A-site substitution in the manganese and iron-containing olivines. This is consistent with the presence in the olivine structure of strong $\sim 120^\circ$ B-O-B nearest-neighbor interactions which dominate the weaker $\sim 90^\circ$ interactions.

High Pressure. Ringwood (1) reported the formation of the spinel Fe_2SiO_4 by pressing Fe, Fe_2O_3 , and $\text{SiO}_2 \cdot \text{H}_2\text{O}$ at 450°C and 55 kb. Akimoto et al. (2,26) have since studied the transformation of the olivine Fe_2SiO_4 to the spinel as a function of temperature and pressure; complete transformations were reported at conditions ranging from 760°C and 46 kb to 1500°C and 75 kb. Under the conditions of this study, it was found that crystalline olivine Fe_2SiO_4 did not transform to the spinel. Attempts were made to carry out the transformation in the presence of water at 50 kb and at temperatures in the range of 400 to 700°C . In addition, transformation was attempted at 50 kb and temperatures up to 1500°C in the absence of water. Failure to obtain a transformation may be a consequence of the high purity of the olivine used. However, transformation was achieved when the samples contained nucleation centers in the form of Fe_2GeO_4 spinel and were squeezed at 400°C and 50 kb for 90 min.

A sample containing the nominal composition $\text{Fe}_2\text{Ge}_{0.3}\text{Si}_{0.7}\text{O}_4$ was chosen for characterization before and after squeezing. The prereacted sample was found to be an olivine-spinel mixture before squeezing. The olivine phase may be assigned the composition $\text{Fe}_2\text{Ge}_{0.2}\text{Si}_{0.8}\text{O}_4$ from the solubility limit of 20 mole percent of the spinel Fe_2GeO_4 in the olivine Fe_2SiO_4 . Likewise, the spinel phase may be assigned the composition Fe_2GeO_4 since less than 10 mole percent of the olivine Fe_2SiO_4 is soluble in the spinel Fe_2GeO_4 . The Weiss constant of a phase mixture in this system can be shown to be equivalent to the sum of the individual products of the Weiss constants with the mole fractions for each component. The above phase assignment for the mixture $\text{Fe}_2\text{Ge}_{0.3}\text{Si}_{0.7}\text{O}_4$ predicts a value for θ of -88K , which agrees with the observed θ value.

Pressing this sample with the nominal composition $\text{Fe}_2\text{Ge}_{0.3}\text{Si}_{0.7}\text{O}_4$ resulted in a dark green product. X-ray examination indicated that the product consisted mostly of a spinel phase corresponding to transformed olivine, some small amounts of Fe_2GeO_4 spinel, and untransformed olivine. Cubic cell parameters were determined for the high pressure spinel phase from both Debye-Scherrer and diffractometer patterns. Good agreement between techniques was obtained with an average value of $a_0 = 8.292(3)\text{\AA}$. This cell parameter lies between $a_0 = 8.406(1)\text{\AA}$ for Fe_2GeO_4 spinel and $a_0 = 8.234(1)\text{\AA}$ reported for Fe_2SiO_4 spinel (1,2).

The Curie-Weiss plots for the nominal composition $\text{Fe}_2\text{Ge}_{0.3}\text{Si}_{0.7}\text{O}_4$ before and after squeezing are shown in Figure 5. The data for the sample after squeezing show curvature at low temperatures, such that the Curie-Weiss parameters (listed in Table II) were determined in the temperature range of 170 to 300K. The values of θ for this sample before and after squeezing are $-88(1)\text{K}$ and $+34(4)\text{K}$, respectively. In the unpressed sample of $\text{Fe}_2\text{Ge}_{0.3}\text{Si}_{0.7}\text{O}_4$, which contains mostly olivine, the antiferromagnetic interactions are stronger than the ferromagnetic interactions; in the pressed sample, which contains mostly spinel, the ferromagnetic interactions are stronger. This is consistent with the presence of strong $\sim 120^\circ$ B-O-B nearest-neighbor interactions in the olivine structure which are not present in the spinel structure. The θ value of $34(4)\text{K}$ for the pressed sample of $\text{Fe}_2\text{Ge}_{0.3}\text{Si}_{0.7}\text{O}_4$ is 66K more positive than the value of $-32(1)\text{K}$ for unsubstituted Fe_2GeO_4 spinel. Upon substitution of silicon for germanium in Fe_2GeO_4 spinel, the ferromagnetic interactions apparently become stronger

than the antiferromagnetic interactions. This is consistent with the presence of both weak ferromagnetic and antiferromagnetic $\sim 90^\circ$ B-O-B interactions of comparable strengths in the spinel structure.

SUMMARY AND CONCLUSIONS

Members of the system $\text{Fe}_2\text{Ge}_x\text{Si}_{1-x}\text{O}_4$ were prepared and their magnetic susceptibilities were measured. The μ_{eff} values for all compositions were consistent with high-spin $\text{Fe}^{2+}(3d^6)$, and θ values were found to be dependent upon the structure and the extent of substitution. The olivine Fe_2SiO_4 showed a θ value of $-87(1)\text{K}$, which was more negative than $-32(1)\text{K}$ for the spinel Fe_2GeO_4 , indicating that the antiferromagnetic interactions are stronger in Fe_2SiO_4 olivine than in Fe_2GeO_4 spinel. At ambient pressure, up to 20 mole percent of germanium was substituted for silicon in the olivine Fe_2SiO_4 . The antiferromagnetic interactions appeared to be insensitive to the substitution of germanium for silicon in the olivine structure, in agreement with the presence of strong $\sim 120^\circ$ antiferromagnetic B-O-B nearest-neighbor interactions which dominate the weaker $\sim 90^\circ$ B-O-B interactions.

When the nominal composition $\text{Fe}_2\text{Ge}_{0.3}\text{Si}_{0.7}\text{O}_4$, containing mostly olivine, was pressed at 50 kb, the resulting product was predominantly a spinel phase. The values of θ for this composition before and after pressing were $-88(1)\text{K}$ and $+34(4)\text{K}$, respectively. This is consistent with the presence of strong antiferromagnetic $\sim 120^\circ$ B-O-B nearest-neighbor interactions in the olivine

structure, which are not present in the spinel structure. The Weiss constant θ was found to be sensitive to the substitution of silicon for germanium within the spinel structure, in agreement with the presence of both weak ferromagnetic and antiferromagnetic $\sim 90^\circ$ B-O-B interactions of comparable strengths.

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TABLE I

Structural Data for $\text{Fe}_2\text{Ge}_x\text{Si}_{1-x}\text{O}_4$

Composition	Structure	$a_o (\text{\AA})$	$b_o (\text{\AA})$	$c_o (\text{\AA})$	$v (\text{\AA}^3)$
Fe_2SiO_4	Olivine	4.821(1)	10.480(1)	6.090(1)	307.7(1)
$\text{Fe}_2\text{Ge}_{0.1}\text{Si}_{0.9}\text{O}_4$	Olivine	4.837(1)	10.489(1)	6.094(1)	309.2(1)
$\text{Fe}_2\text{Ge}_{0.2}\text{Si}_{0.8}\text{O}_4$	Olivine	4.853(1)	10.499(1)	6.099(1)	310.8(1)
Fe_2GeO_4	Spinel	8.406(1)			
$\text{Fe}_2\text{Ge}_{0.3}\text{Si}_{0.7}\text{O}_4^a$	Spinel	8.292(3)			

a) Nominal Composition

TABLE II

Magnetic Susceptibility Data for $\text{Fe}_2\text{Ge}_x\text{Si}_{1-x}\text{O}_4$

<u>Composition</u>	<u>Structure</u>	<u>$\mu_{\text{eff}}(\mu_B)$</u>	<u>θ (K)</u>
Fe_2SiO_4	Olivine	5.22(2)	-87(1)
$\text{Fe}_2\text{Ge}_{0.1}\text{Si}_{0.9}\text{O}_4$	Olivine	5.29(2)	-93(1)
$\text{Fe}_2\text{Ge}_{0.2}\text{Si}_{0.8}\text{O}_4$	Olivine	5.26(1)	-96(1)
$\text{Fe}_2\text{Ge}_{0.3}\text{Si}_{0.7}\text{O}_4^a$	Olivine	5.16(1)	-88(1)
Fe_2GeO_4	Spinel	5.39(4)	-32(2)
$\text{Fe}_2\text{Ge}_{0.3}\text{Si}_{0.7}\text{O}_4^a$	Spinel	5.24(3)	+34(4)

a) Nominal Composition

REFERENCES:

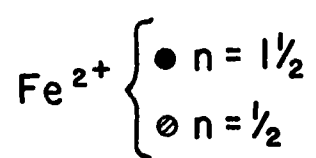
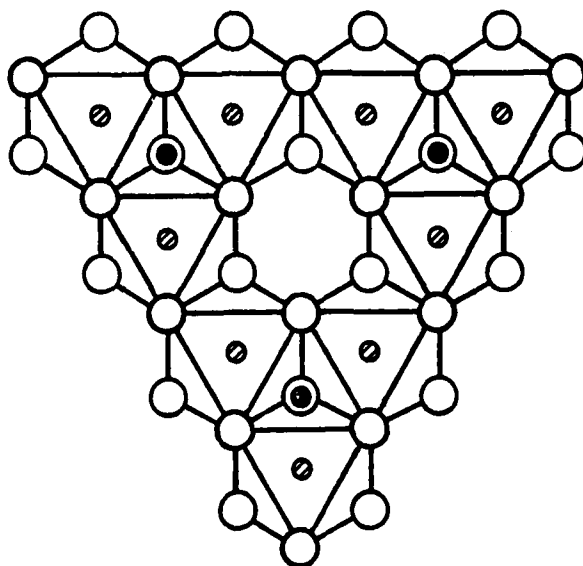
1. A.E. Ringwood; *Geochim. Cosmochim. Acta* 15, 18 (1958).
2. S. Akimoto, H. Fujisawa, and T. Katsura; *J. Geophys. Res.* 70, 1969 (1965).
3. A.E. Ringwood; *Nature* 198, 79 (1963).
4. A.E. Ringwood; *Nature* 178, 1303 (1956).
5. A.E. Ringwood and M. Seabrook; *Nature* 193, 158 (1962).
6. A.E. Ringwood; *Australian J. Sci.* 23, 378 (1961).
7. A. Navrotsky, *J. Solid State Chem.* 16, 185 (1976).
8. M. Inagaki, T. Ozeki, H. Furuhashi, and S. Naka, *J. Solid State Chem.* 20, 169 (1977).
9. A. Durif-Varambon, E.F. Bertaut, and R. Pauthenet; *Ann. Chim. (Paris)* 13, 526 (1956).
10. A.E. Ringwood and A.F. Reid; *J. Phys. Chem. Solids* 31, 2791 (1970).
11. A.E. Ringwood; *Geochim. Cosmochim. Acta* 26, 457 (1962).
12. V. Hariya and C.M. Wai; *J. Fac. Sci., Hokkaido Univ., Ser. 1*, 14, 355 (1970).
13. H. Kondo and S. Miyahara, *J. Phys. Soc. Japan* 18, 305 (1963).
14. R.P. Santoro, R.E. Newnham, and S. Nomura; *J. Phys. Chem. Solids* 27, 655 (1966).
15. F. Hartmann-Boutron; *C.R. Acad. Sci. Paris.* 263B, 188 (1966).
16. G. Blasse and J.F. Fast; *Philips Res. Repts.* 18, 393 (1963).
17. P. Strobel, F.P. Koffyberg, and A. Wold; *J. Solid St. Chem.* 31, 209 (1980).
18. H.T. Hall; *Rev. Sci. Instrum.* 31, 125 (1960).
19. B.L. Morris and A. Wold; *Rev. Sci. Instrum.* 89, 1937 (1968).
20. C.M. Sung and R.G. Burns; *Phys. Chem. Miner.* 2, 177 (1978).
21. G. Blasse; *Bull. Soc. Chim. France* 4, 1212 (1965).

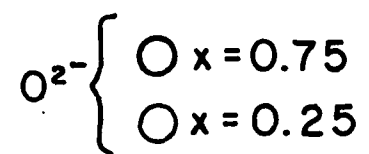
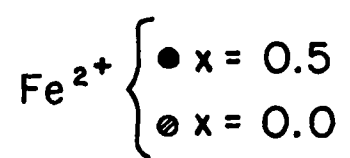
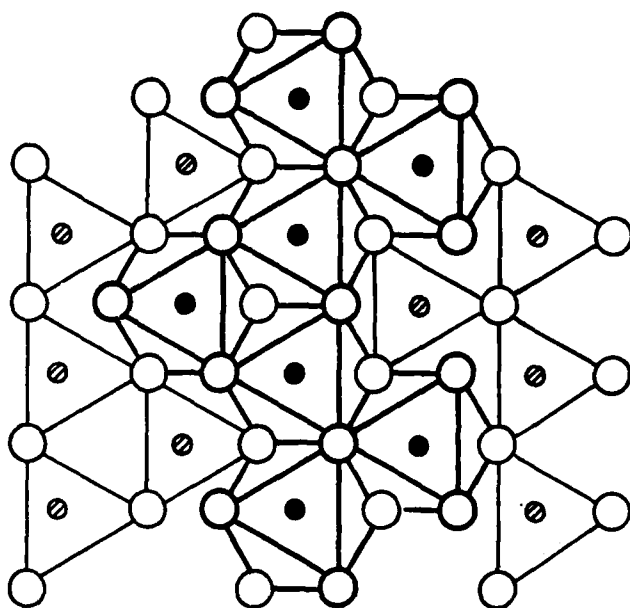
REFERENCES (Continued)

22. J.B. Goodenough; Phys. Rev. 117, 1442 (1960).
23. J.B. Goodenough; "Magnetism and the Chemical Bond," Krieger, New York 1976.
24. P.W. Selwood, "Magnetochemistry," 2nd ed., Interscience, New York, 1956.
25. J.G. Creer and J.G.F. Troup; Solid St. Commun. 8, 1183 (1970).
26. T. Yagi, F. Marumo, and S. Akimoto; Am. Miner. 59, 486 (1974).

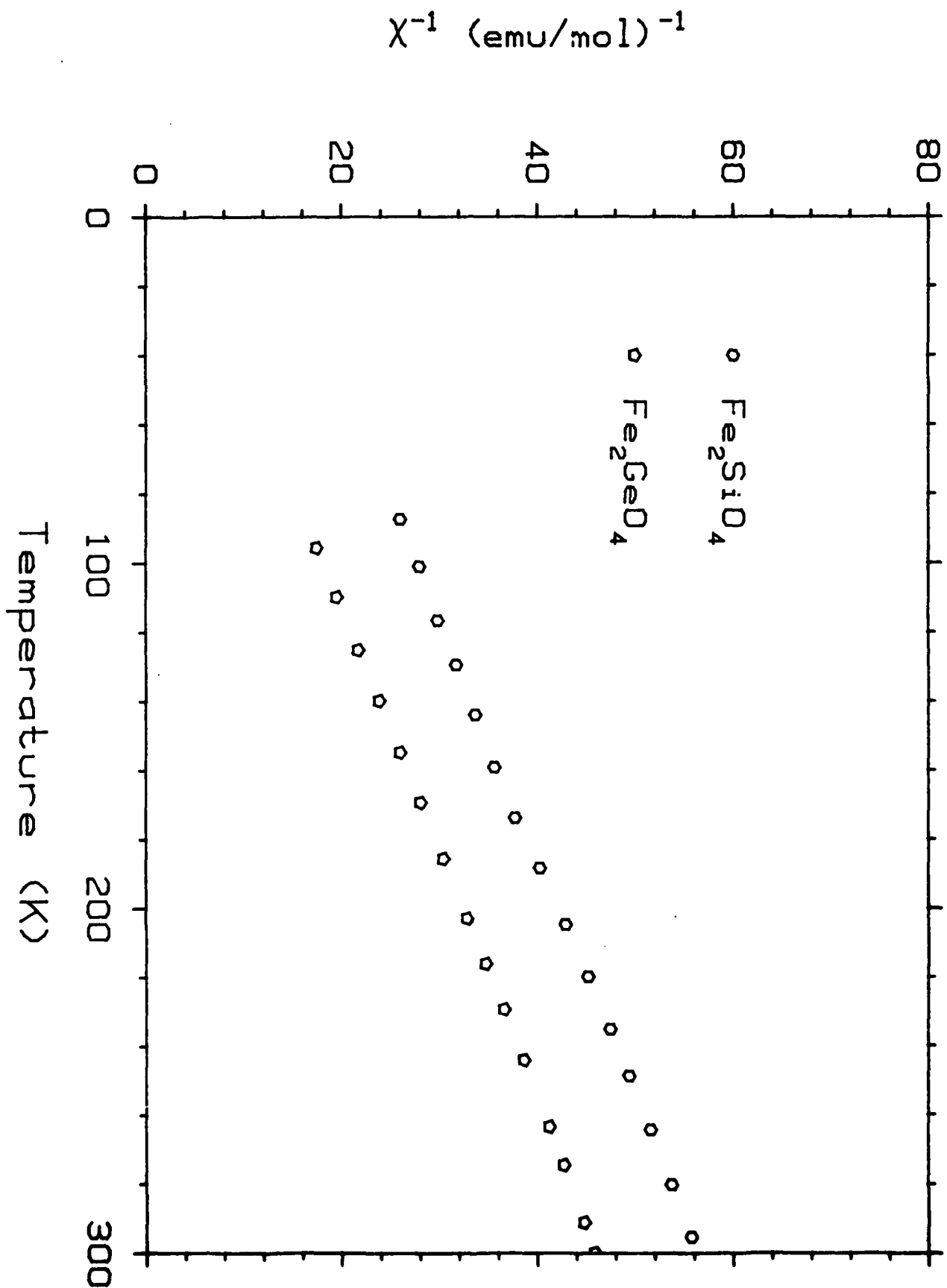
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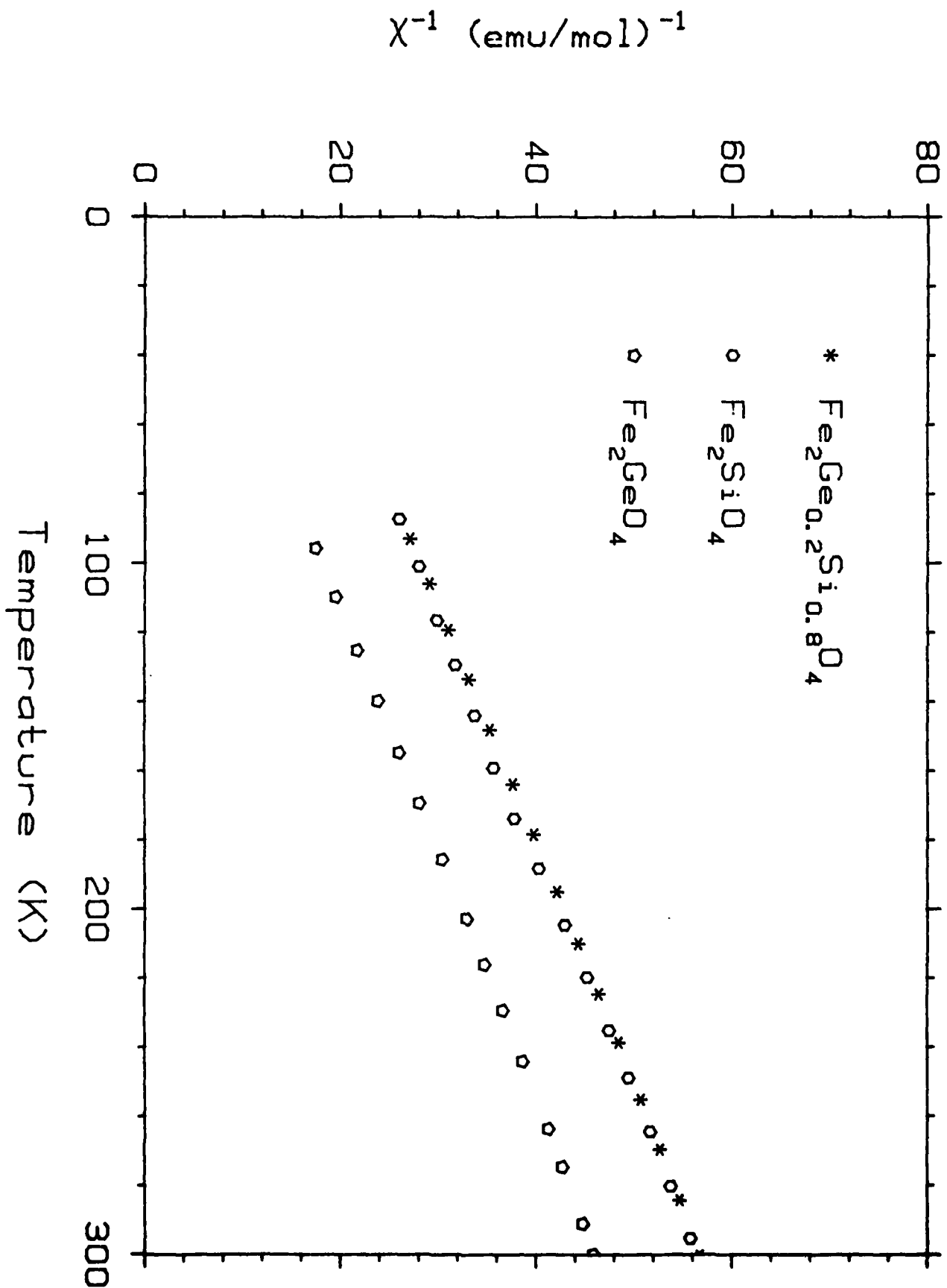
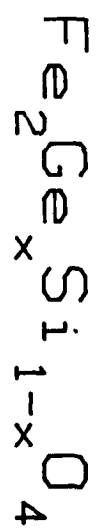
- Figure 1 The spinel structure. The arrangement of B-sites above and between two layers of close-packed O^{2-} anions, projected along $[111]$. $n = \sqrt{3}a_0/6$ is the distance between layers.
- Figure 2 The olivine structure. The arrangement of B-sites below and between two layers of close-packed O^{2-} anions, projected along $[100]$.
- Figure 3 Inverse magnetic susceptibility versus temperature for the olivine Fe_2SiO_4 and the spinel Fe_2GeO_4 .
- Figure 4 Inverse magnetic susceptibility versus temperature for the olivines Fe_2SiO_4 and $Fe_2Ge_{0.2}Si_{0.8}O_4$ and the spinel Fe_2GeO_4 .
- Figure 5 Inverse magnetic susceptibility versus temperature for the nominal composition $Fe_2Ge_{0.3}Si_{0.7}O_4$ in both its predominantly olivine and spinel forms.

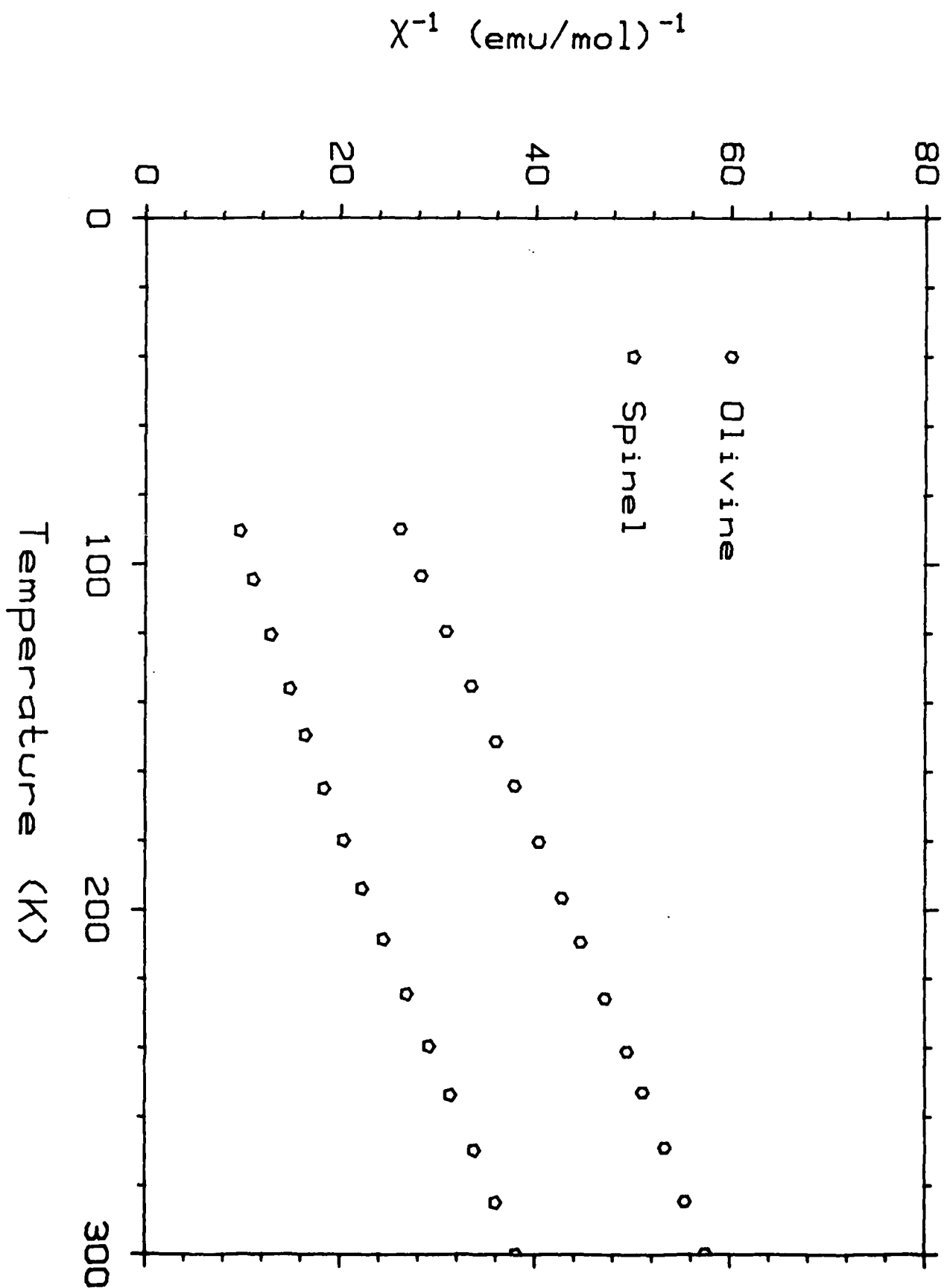
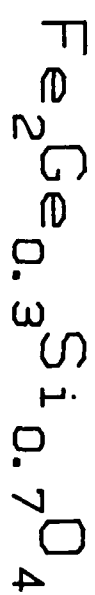




Fe_2SiO_4 vs. Fe_2GeO_4







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